

On nonadiabatic calculation of dipole moments

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We show that a recent non Born–Oppenheimer calculation of dipole moments exhibits obscure points and is not consistent with the well known Hellmann–Feynman theorem.

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I. INTRODUCTION

Some time ago Cafiero and Adamowicz[1] calculated the dipole moments of LiH and LiD without resorting to the Born–Oppenheimer (BO) approximation. Their approach consists in the expansion of the eigenfunction of the Coulomb Hamiltonian in a basis set of floating s-type explicitly correlated Gaussian functions[1]. The dipole moments obtained in this way are essentially identical to the experimental values[2] and the authors claim that their calculations simulate experiment more closely than any previous ones[1]. They also applied basically the same approach to the calculation of molecular polarizabilities[3, 4, 5].

The purpose of this paper is to analyze that non Born–Oppenheimer calculation of dipole moments of diatomic molecules in the light of the Hellmann–Feynman theorem[6]. In Section II we outline some well known properties about the molecular Hamiltonian that are necessary for the remaining sections, in Section III we develop the Hellmann–Feynman theorem for optimized variational wave functions, in Section IV we apply it to the calculation of dipole moments described by Cafiero and Adamowicz[1] and in Section V we draw conclusions and summarize the main results of this paper.

II. PRELIMINARIES

In this section we outline some well known properties of the molecular Hamiltonian that are necessary for present discussion of the nonadiabatic calculation of dipole moments. A more detailed analysis was provided earlier by other authors[7, 8]. Following Cafiero and Adamowicz[1] we consider a nonrelativistic Coulomb Hamiltonian of the form[7, 8]

$$\hat{H}_T = \sum_i \frac{\hat{p}_i^2}{2m_i} + \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where m_i , q_i and \hat{p}_i are the mass, charge, and momentum, respectively, of particle i located at position \mathbf{r}_i , $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between particles i and j , and ϵ_0 is the vacuum permittivity. The first step in the treatment of such system of particles is the separation of the motion of the center of mass which we carry out by means of the linear transformation

$$\mathbf{r}'_i = \sum_j t_{ij} \mathbf{r}_j \quad (2)$$

so that the Hamiltonian operator (1) becomes

$$\hat{H}_T = \sum_j \sum_k \left(\sum_i \frac{t_{ji} t_{ki}}{m_i} \right) \hat{p}'_j \hat{p}'_k + \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} = \hat{H}_M + \hat{H}_{CM} \quad (3)$$

where \hat{p}'_i is the momentum conjugate to \mathbf{r}'_i . In this way we remove the motion of the center of mass given by \hat{H}_{CM} and are left with the translation-free molecular Hamiltonian \hat{H}_M provided we choose the transformation matrix elements t_{ij} conveniently[7, 8].

Following Cafiero and Adamowicz[1] we can choose $\mathbf{r}'_1 = \mathbf{r}_{CM}$ and $\mathbf{r}'_j = \mathbf{r}_j - \mathbf{r}_1$, $j > 1$, where \mathbf{r}_{CM} and \mathbf{r}_1 denote the positions of the center of mass and the heaviest nucleus in the molecule, respectively. Other authors have proposed a more symmetric transformation: $\mathbf{r}'_1 = \mathbf{r}_{CM}$ and $\mathbf{r}'_j = \mathbf{r}_j - \mathbf{r}_{NCM}$, where \mathbf{r}_{NCM} is the position of the center of mass of the nuclei[9]. In this case the coordinates of the nuclei are not independent and one of them can be expressed in terms of the others[9]. One advantage of the transformation chosen by Cafiero and Adamowicz[1] is that the form of the potential-energy function remains simple because $r_{j1} = |\mathbf{r}'_j|$ and $r_{ij} = |\mathbf{r}'_i - \mathbf{r}'_j|$, $i, j > 1$.

The inversion operator \hat{i} changes the sign of the coordinates and momenta of all the particles: $\hat{i}\mathbf{r}_j\hat{i}^{-1} = -\mathbf{r}_j$, $\hat{i}\hat{p}_j\hat{i}^{-1} = -\hat{p}_j$, where $\hat{i}^{-1} = \hat{i}$. It is clear that the translation-free Hamiltonian operator is invariant under inversion $\hat{i}\hat{H}_M\hat{i}^{-1} = \hat{H}_M$. Therefore, if ψ and E are an eigenfunction and its eigenvalue, respectively, of \hat{H}_M then $\hat{i}\hat{H}_M\psi = \hat{H}_M\hat{i}\psi = E\hat{i}\psi$. If the state is nondegenerate we conclude that $\hat{i}\psi = \pm\psi$ because $\hat{i}^2 = \hat{1}$ (the identity operator). In particular, the ground state is nondegenerate and spherically symmetric[7, 8, 10].

The classical dipole moment for a neutral distribution of charges is given by the well-known expression

$$\mu = \sum_j q_j \mathbf{r}_j \quad (4)$$

It follows from $\hat{i}\mu\hat{i}^{-1} = -\mu$ and what was said above that $\langle\psi|\mu|\psi\rangle = 0$ for any nondegenerate molecular state. In other words, the outcome of the quantum-mechanical nonadiabatic calculation of the dipole moment as the expectation value of the corresponding operator is zero for any molecule in its ground state. In order to circumvent this difficulty, Cafiero and Adamowicz considered the classical interaction between the dipole moment and the field ϵ thus obtaining the semiclassical Hamiltonian

$$\hat{H}_\epsilon = \hat{H}_M - \epsilon \cdot \mu \quad (5)$$

that behaves as $\hat{i}\hat{H}_\epsilon(\epsilon)\hat{i}^{-1} = \hat{H}_\epsilon(-\epsilon)$. If we choose ϵ along the z axis, $\epsilon = (0, 0, \epsilon)$, then $\epsilon \cdot \mu = \epsilon\mu_z$. If ψ_ϵ and E_ϵ are an eigenfunction and its eigenvalue, respectively, of \hat{H}_ϵ we have $\hat{i}\hat{H}_\epsilon(\epsilon)\psi_\epsilon = \hat{H}_\epsilon(-\epsilon)\hat{i}\psi_\epsilon = E_\epsilon\hat{i}\psi_\epsilon$. Consequently, if the state is nondegenerate then the energy is an even function of the field: $E_\epsilon(-\epsilon) = E_\epsilon(\epsilon)$.

Throughout this paper we omit the fact that the Hamiltonian operator (5) does not support bound states because it was not an issue in the nonadiabatic calculation of molecular dipole moments and polarizabilities[1, 3, 4, 5].

III. THE HELLMANN-FEYNMAN THEOREM

In what follows we briefly discuss the Hellmann-Feynman theorem for variational wave functions[6] because the nonadiabatic calculation of dipole moments has necessarily been based on them. Consider a trial function Φ that

depends on a set of adjustable parameters $\mathbf{a} = \{a_1, a_2, \dots, a_n\}$. If we differentiate the variational energy $E(\mathbf{a})$ given by

$$E \langle \Phi | \Phi \rangle = \langle \Phi | \hat{H} | \Phi \rangle \quad (6)$$

with respect to the variational parameters and require that

$$\left(\frac{\partial E}{\partial a_i} \right)_{\mathbf{a}=\mathbf{a}^{opt}} = 0, \quad i = 1, 2, \dots, n \quad (7)$$

then the optimal trial function satisfies

$$\left\langle \frac{\partial \Phi}{\partial a_i} \left| \hat{H} - E \right| \Phi \right\rangle_{\mathbf{a}=\mathbf{a}^{opt}} + \langle \Phi | \hat{H} - E \left| \frac{\partial \Phi}{\partial a_i} \right\rangle_{\mathbf{a}=\mathbf{a}^{opt}} = 0, \quad i = 1, 2, \dots, n \quad (8)$$

Suppose that the Hamiltonian operator \hat{H} depends on a parameter λ (which may be a particle charge or mass, the intensity of an applied field, etc). The optimized variational function will depend on λ through the optimal parameters \mathbf{a}^{opt} . Therefore, if we differentiate equation (6) with respect to λ

$$\frac{\partial E}{\partial \lambda} \langle \Phi | \Phi \rangle = \sum_{i=1}^n \left(\left\langle \frac{\partial \Phi}{\partial a_i} \left| \hat{H} - E \right| \Phi \right\rangle + \langle \Phi | \hat{H} - E \left| \frac{\partial \Phi}{\partial a_i} \right\rangle \right) \frac{\partial a_i}{\partial \lambda} + \langle \Phi | \frac{\partial \hat{H}}{\partial \lambda} | \Phi \rangle \quad (9)$$

and take into account the variational expression (8) then we prove that the optimized variational function satisfies the well known Hellmann–Feynman theorem[6]:

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle \quad (10)$$

where $\langle \hat{A} \rangle = \langle \Phi | \hat{A} | \Phi \rangle / \langle \Phi | \Phi \rangle$. Of course, any eigenfunction of \hat{H} and its corresponding eigenvalue satisfy this relationship.

IV. NONADIABATIC CALCULATION OF DIPOLE MOMENTS

In order to calculate the dipole moment of the diatomic molecule Cafiero and Adamowicz[1] fitted three points of the energy curve $E_\epsilon(\epsilon)$ with a second-degree polynomial and obtained μ_z from the coefficient of the linear term.

$$E_\epsilon(\epsilon) \approx e_0 + e_1\epsilon + e_2\epsilon^2 + \dots \quad (11)$$

They resorted to polynomials of higher degree in other calculations[3, 4, 5].

According to the Hellmann–Feynman theorem (10) we expect that

$$\frac{\partial E_\epsilon}{\partial \epsilon} = - \langle \hat{\mu}_z \rangle_\epsilon \quad (12)$$

for the kind of variational function that Cafiero and Adamowicz[1] chose to solve the Schrödinger equation approximately. Consequently,

$$\left. \frac{\partial E_\epsilon}{\partial \epsilon} \right|_{\epsilon=0} = e_1 = - \langle \hat{\mu}_z \rangle_0 = 0 \quad (13)$$

unless the variational function is not fully optimized or it does not recover the correct symmetry as $\epsilon \rightarrow 0$. This result is consistent with the argument of Section II that $E_\epsilon(\epsilon)$ is an even function of ϵ .

The simple arguments outlined above clearly show that a nonadiabatic calculation, either as an expectation value or by fitting the energy with a polynomial function of the field intensity should produce the only result of zero dipole moment. However, Cafiero and Adamowicz[1] managed to obtain the dipole moments of the diatomic molecules by means of the following “trick”:[1] “The energy was calculated for each basis with three electric field strengths, $\epsilon_z = 0, -0.0016$, and -0.0032 a.u., and the energy curve was fitted with a second order polynomial in ϵ_i . μ is then the first order coefficient of this fit.” In fact, the theoretical dipole moments estimated in this curious way appear to converge smoothly towards the experimental ones as the number of basis functions increases[1]. Later they explained this procedure in a more detailed way[4]: “We use the finite field approach in the present work, i.e., we calculate the energies of the system for several field strengths, we fit the energy as a function of the field strength with a polynomial, and last we use the polynomial to determine the energy derivatives with respect to the field at the zero field. As is clear from the discussion above, the non-BO energy of a molecule at the field strength f is identical to the energy at the field $-f$, because when the direction of the field changes the orientation of the molecule follows the field direction. Thus, for any system in the H_2 isotopomer series the energy is an even function of the field, and if it is approximated by a polynomial, only even powers need to be used. This obviously results in a zero dipole for any system if the dipole moment is determined as described above. An alternative approach is to apply stronger fields and only use energies calculated for positive field strengths in generating the polynomial fit. In this case the use of both even and odd powers is appropriate. As we have shown in our previous work on LiH[1], the dipole moment derived from our non-BO calculations with the procedure that uses only positive fields and polynomial fits with both even and odd powers match very well the experimental results. Thus in the present work we will show results obtained using interpolations with even and odd-power polynomials.” Summarizing: Cafiero and Adamowicz[1, 4] tells us that it is possible to fit an even function by means of a polynomial one with even and odd powers of the variable provided one chooses sufficiently great values on the positive side of the variable axis. It is clear that the nonzero coefficients of the odd powers should be the product of numerical errors. Otherwise, if we apply this argument to, for example, $\cos(f)$, then we will prove that $\sin(0) \neq 0$. A question arises: if the outcome of the linear term in the expansion of the energy as a function of the electric-field intensity was due to numerical errors, why did the dipole moments estimated by Cafiero and Adamowicz[1] agreed so accurately with the experimental ones?. Notice that this same “trick” led to negligible dipole moments for the A_2 diatoms[4] which is consistent with the classical view that they should have zero dipole moments: “Applying the same approach to homonuclear species (H_2 , D_2 , and T_2) should give the dipoles identically equal to zero. In our calculations, these actually come out to 10^{-8} . This small noise which entered our calculations was due in part to the previously mentioned fact that the zero-field wave function we use is not an eigenfunction of \hat{J}^2 as it should be. The level of noise introduced is negligible, as 10^{-8} is 4 orders of magnitude smaller than the size of the dipole moments for the heteronuclear species.”

It seems that Cafiero and Adamowicz[1] chose suitable trial wave functions for the calculation of the dipole moments that did not reflect the expected symmetry of the exact eigenfunctions at zero field strength (otherwise the linear term of the polynomial (11) would have been zero). The success of their calculation was probably due to the particular placement of the floating Gaussian functions that reflects the ionic character of the chemist’s classical picture of the molecules:[1] “Thus the centers corresponding to the hydrogen nucleus were scattered from about 2.9 to about 3.1 bohrs. The lithium nucleus was, of course, placed at the origin of the internal coordinate system. The functional centers corresponding to the electrons were located primarily on the two nuclei, with two electrons at the origin (about

0.0 ± 0.001 bohrs in all three directions) and two electrons near the H nucleus (about 3.05 ± 0.06 bohrs) per basis set. This reflects the strong ionic character in the lithium/hydrogen bond. The LiD non-BO wave function was optimized starting from the converged LiH wave function.” Therefore, it is not clear that the variational wavefunction reflects the correct symmetry of the system for the values of the electric-field intensity chosen for the fit. If the variational functions were allowed to approach the symmetry of the exact eigenfunctions of $\hat{H}_{\epsilon \rightarrow 0} = \hat{H}_M$ as the field vanishes, the linear terms of the fitting polynomials would be zero as well as the predicted dipole moments[10]. This may probably be the case of the homonuclear diatoms[4].

V. CONCLUSIONS

When the field is on, the wavefunction no longer have spherical symmetry, the expectation value of $\hat{\mu}$ is nonzero and depends on the field strength ϵ . However, it is well-known that $E_\epsilon(-\epsilon) = E_\epsilon(\epsilon)$ and the expansion of the energy about $\epsilon = 0$ should exhibit only even powers of the field strength (as we have briefly shown in Section II). In other words, the linear term should be zero in agreement with the Hellmann–Feynman theorem (13).

We have shown that if one allows the optimized variational wave function to recover the correct spherical symmetry when the field intensity vanishes then the linear term of the polynomial (11) should be zero as well as the predicted dipole moment. Apparently, the optimized variational wave function used by Cafiero and Adamowicz[1, 3, 4, 5] retains, when $\epsilon \rightarrow 0$, the cylindrical symmetry it has for $\epsilon > 0$. This may be due to the particular placement of the floating gaussians in space. Another hint was given by Cafiero et al[11]: “Since the basis functions used here are eigenfunctions of \hat{J}_z but not \hat{J}^2 , they are of correct symmetry only for the non-zero-field calculations. In order to maintain equal representation of all the points in the fit, though, they are used for the zero field point as well. This should introduce only mild contamination by excited rotational states and has not been a practical problem in the past.” However, that contamination may be the cause of the occurrence of the linear term in the fit of $E_\epsilon(\epsilon)$. For that reason, we believe that the apparent success of the approach proposed by Cafiero and Adamowicz[1, 3, 4, 5] should be further investigated.

It is clear from the following referee’s comment that this problem is not well understood: “There is no spherical symmetry when the electric field is included, thus there is no inconsistency in the calculations of Cafiero and Adamowicz in this respect.” However, from the arguments already given above it is clear that the coefficient of the linear term should be the expectation value of $\hat{\mu}_z$ at zero field strength that obviously corresponds to a spherical-symmetric ground-state. The referee is one of the supporters that $\sin(0) \neq 0$.

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